Supplementary Information

A Facile and Visual Approach for Trace level Ammonia vapour Detection under Ambient Conditions

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1. General Information

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1. General Information

Experimental spectra (¹H, ¹⁹F, and ¹¹B NMR), were recorded using a Bruker instrument operating at 500 MHz, 376 MHz and 128 MHz respectively. UV/Vis spectra were recorded on Shimadzu spectrophotometry UV-1800. Fluorescence emission spectra were recorded on a Horiba Jovin Vyon Fluoro log 3-111 spectrophotometer. The measurements of spontaneous fluorescence decay were done on time-correlated single-photon counting (TCSPC) system from HORIBA. Molecules were excited at their maximum absorption signal using N-470L picosecond diodes (IBH-NanoLed) and emission was collected at magic angle polarization using a Hamamatsu MCP photomultiplier (Model R-3809U-50). The TCSPC setup consists of an Ortec 9327 pico-timing amplifier. The data was collected with a PCI-6602 interface card as a multi-channel analyzer. Graph plotting and liner-curve fitting was done in Origin Pro 8.

For the determination of the relative fluorescence quantum yields (\emptyset s), dilute solutions of compounds with an absorbance < 0.2 near excitation wavelengths were used. The \emptyset s of compounds were calculated using Rhodamine 6G (standard, \emptyset r = 0.95) as fluorescence standards with the help of below expression:

Where $\emptyset s$ and $\emptyset r$ are the emission quantum yields of sample and reference standard respectively, f(S), A(S), A(r) and f(r) indicate the fluorescence area of sample, epsilon value of sample, epsilon value and fluorescence area of standard respectively.

Single crystal data was collected on a Bruker APEX II diffractometer equipped with a graphite monochromator and Mo-K α ($\lambda = 0.71073$ Å) radiation. Data collection was

performed using φ and ω scans. The structures was solved using direct method followed by full matrix least square refinements against F2 (all data HKLF 4 format) using SHELXTL. All calculations were carried out using SHELXL 97, PLATON 99, and WinGXsystemVer-1.6414. CCDC 1060713, contain the supplementary crystallographic data for this paper.¹⁻³

Cyclic voltametry (CV) measurements were carried out using CH potentiostat from CHI Instruments. CV experiments were done under continuous argon flow and three electrode electrochemical cell was used. A glassy carbon working a platinum wire counter with Ag/Ag^+ as reference electrode was used. All the measurements were done in THF and CH₃CN solution with 0.1 M TBAP as a supporting electrolyte. All the spectra were recorded at a scan rate of 0.1 V/s.

All density functional (DFT) and time-dependent functional (TD-DFT) calculations were conducted using Gaussian 09 of programs. In the DFT calculation, solvent correction was incorporated with the help of IEFPCM model using CH₃CN solvent.

2. TCSPC data (S1)



Figure 1. TCSPC decay profile of compound 1 (left) and 2 (right).

3. Experimental and Theoretical Absorption Spectra (S2)



Figure 2. Comparison of experimental and theoretical absorption spectra (TD-DFT) for compound 2.

4. Synthesis and Characterization of 2 (S3)

Compound **1** (200 mg, 0.427 mmol) was dissolved in 10 ml of absolute ethanol. 5 ml of 2 M aqueous solution of ammonia was added to it, under room temperature conditions (Scheme 1). The progress of reaction was monitored by thin layer chromatography and UV-Vis. After half an hour, reaction was completed and the reaction mixture was evaporated under reduced pressure. The crude product obtained was subjected to silica gel (100-200 mesh) column chromatography with CH₂Cl₂/hexane (2/1, v/v) as eluent. The product (**2**) was recrystallized with CH₂Cl₂/hexane and dried. The obtained product appeared like reddish powder and characterized (90% yield). ¹H NMR (500 MHz; DMSO-D₆; Me₄Si, 298 K): δ 9.30 (s, 1H), δ 8.54 (s, 1H), δ 7.19 (d, *J*=5.1 Hz, 1H), δ 6.45 (d, *J*=5.15 Hz, 1H), δ 6.30 (d, *J*=3.7 Hz, 1H), δ 6.26 (d, *J*=3.65 Hz, 1H). ¹⁹F NMR (376 MHz, CDCl₃): δ = -136.51 (m, 2F, ortho *Ph-F*), δ = -146.88 (dd, ¹*J*_{F-B} = *55.44* Hz, ¹*J*_{F-B} = *27.2* Hz, 2F, BF₂), δ = -148.45. (m, 1F, para *Ph-F*), δ - 158.14 (m, 2F, meta *Ph-F*). ¹¹B NMR (128 MHz): δ 0.64 (t, ¹*J*_{B-F} = 32.2.00 Hz, 1B, BF₂).



Scheme 1. Synthesis of compound 2.

¹H NMR spectrum of **2** in DMSO-d₆ at 25° C.



 ^{19}F NMR spectrum of **2** in CDCl₃ at 25°C.



¹¹B NMR spectrum of **2** in CDCl₃ at 25°C.



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5. Calibration Curves (S4)



Figure 3. (a) Variation of absorption of dye solution (1) in CH₃CN at 463 nm with various concentrations of ammonia vapour. (b) Emission intensity of dye solution (1) in CH₃CN at 530 nm at various concentrations of ammonia vapour. The ammonia vapours were released from aqueous ammonia solution under room temperature conditions. Here the concentration of BODIPY dye molecule used is 10 μ M for absorption and emission mode calculations.

6. References

 (a) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J.Gaussian 09, Revision A. 02; Gaussian, Inc., Wallingford CT, **2009**.

2. (a) Polster, J.; Lachmann, H. Spectrometric Titrations. VCH: Weinheim, **1989**. (b) Connors, K. A. *Binding Constants. The Measurement of Molecular Complex*. Wiley: New York, **1987**. (c) Benesi, H. A.; Hildebrand, J. H. *J. Am. Chem. Soc.* **1949**, *71*, 2703.

3. (a) Chutia, R.; Das, G. *Dalton. Trans.* 2014, *43*, 15628. (b) Boiocchi, M.; Del, B. L.;
Gomez, D. E.; Fabbrizzi, L.; Licchelli, M.; Monzani, E. *J. Am. Chem. Soc.* 2004, *126*, 16507.
(c) Politzer, P.; Lane, P.; Concha, M. C.; Ma. Y.; Murray, J. S. *J. Mol. Model.* 2007, *13*, 305.
(d) Davson, R.; Cooper, A. I.; Adams, D. J. *Org. Biol. Chem.* 2010, *8*, 100.